

FISCHER-TROPSCH-TYPE PRODUCTION OF ORGANIC MATERIALS IN THE SOLAR NEBULA: STUDIES USING GRAPHITE CATALYSTS AND MEASURING THE TRAPPING OF NOBLE GASES.

Joseph A. Nuth III,¹ Frank T. Ferguson^{2,1}, Christopher Lucas^{3,1}, Yuki Kimura⁴ and Charles Hohenberg⁵, ¹Code 691, Astrochemistry Lab, NASA's Goddard Space Flight Center, Greenbelt MD 20771 (Joseph.A.Nuth@NASA.gov)

²Chemistry Department, Catholic University of America, Washington DC, ³University Space Research Association, Columbia MD, ⁴Department of Earth and Planetary Materials Science, Graduate School of Science, Tohoku University, Aoba 6-3, Aoba-ku, Sendai 980-8578 Japan, ⁵Physics Department, Washington University, St. Louis MO

Introduction: The formation of abundant carbonaceous material in meteorites is a long standing problem [1] and an important factor in the debate on the potential for the origin of life in other stellar systems [2]. Many mechanisms may contribute to the total organic content in protostellar nebulae, ranging from organics formed via ion-molecule and atom-molecule reactions in the cold dark clouds from which such nebulae collapse [3], to similar ion-molecule and atom-molecule reactions in the dark regions of the nebula far from the proto star [4], to gas phase reactions in subnebulae around growing giant planets [5] and in the nebulae themselves [6]. The Fischer-Tropsch-type (FTT) catalytic reduction of CO by hydrogen was once the preferred model for production of organic materials in the primitive solar nebula [1,7,8]. The Haber-Bosch (HB) catalytic reduction of N₂ by hydrogen was thought to produce the reduced nitrogen found in meteorites. However, the clean iron metal surfaces that catalyze these reactions are easily poisoned via reaction with any number of molecules, including the very same complex organics that they produce [9] and both reactions work more efficiently in the hot regions of the nebula. Both of these problems may now be moot.

We have demonstrated that many grain surfaces can catalyze both FTT and HB-type reactions, including amorphous iron and magnesium silicates, pure silica smokes as well as several minerals [10]. Although none work as well as pure iron grains, and all produce a wide range of organic products rather than just pure methane, these materials are not truly catalysts. The properties of these surfaces change during the course of reaction and become more efficient as the reaction proceeds to build up a macromolecular grain coating that would usually serve to shut down such activity [11]. Indeed amorphous iron silicate smokes that had accumulated a coating comprising 10% by mass carbon and 0.2% by mass nitrogen based on the total mass of the sample, remained an active and very efficient surface for production of nitrogen-bearing organic materials from a mixture of CO, N₂ and H₂. More recent work may provide a simple explanation for these observations: the carbonaceous grain coating is itself an

efficient surface for the reduction of CO and N₂ by hydrogen to form a variety of organic materials.

Experimental Description: Llorca and Casanova [12] demonstrated that FTT reactions occur under low pressures typical of the primitive solar nebula. Our experiments were designed to produce mixtures of solids and organics to serve as analogs of primitive asteroidal material. Grains in protostellar nebulae are exposed to the ambient gas for tens of thousands of years at pressures ranging from 10⁻³ to 10⁻⁴ atm or less. We do not have such times available for laboratory experiments, although we can duplicate the total number of collisions a grain might experience with components of the ambient gas by running experiments for shorter times at higher pressures. In our laboratory, experiments last from about 3 days at temperatures of 873K to more than a month at temperatures of 573K. If an average experiment lasts a week (6.05 x 10⁵s) then we simulate two centuries (6.3 x 10⁹s) of exposure to an ambient gas at 10⁻⁴ atm. by experiments at ~1 atmosphere. Although higher pressures could effect products synthesized in our experiments, we believe that the effects of temperature are much more important.

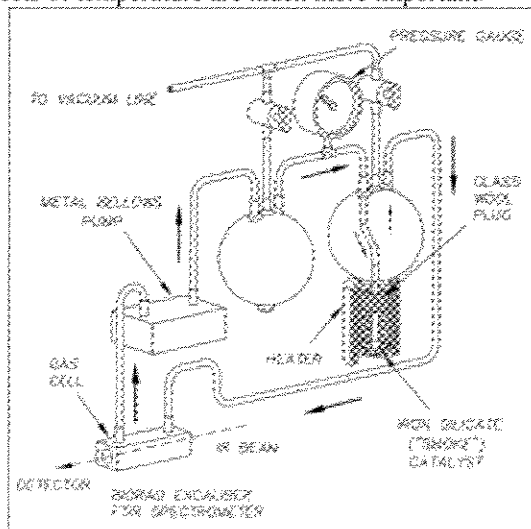


Figure 1. Simple experimental apparatus used to circulate reactive gas mixtures over potential catalysts at controlled temperatures and monitor the changes in the circulating gas via infrared spectroscopy.

The experiments were very simple, see Figure 1 [13]. We load ~25 cm³ of catalyst into a glass finger through which gas can circulate by means of a glass tube that extends to the bottom of the finger. The finger is heated via an external mantle to a controlled temperature. We evacuate the system to a pressure less than ~0.1 torr, then fill the system with gas (75 torr CO, 75 torr N₂, 550 torr H₂) to a total pressure of 700 torr. In the case of experiments to measure the trapping efficiency of noble gases we also add 25 torr of a mixture of noble gases (49% Ne, 49% Ar, 1% Kr, 1% Xe) to a total pressure of 725 torr. We now begin to circulate gas using a bellows pump, begin heating the finger containing the catalyst and record our first infrared spectrum of the gas (only CO is detected in this spectrum) using an FTIR spectrometer. The gas fluidizes the catalyst. The finger is plugged at the top of the heater using glass wool to contain the grains while letting the gas circulate. As the experiment proceeds we use periodic FTIR spectra to follow the loss of CO and the formation of methane, water and carbon dioxide and monitor smaller spectral features due to ammonia and N-Methyl Methylene Imine. Once the CO has been reduced to about ten percent of its starting concentration we take a final infrared spectrum, turn off the heater, cool the system to room temperature, evacuate it to less than ~0.1 torr, then refill the system with fresh gas and begin a second run. Note that we do not use a fresh batch of catalyst for this second run. By making ~15 runs with the same catalyst, we simulate ~3000 years of exposure of grains to nebular gas and build up a substantial coating of macromolecular carbon, nitrogen (and hydrogen).

Results for Graphite Catalyst: Graphite is not a particularly good FTT catalyst, especially compared to iron powder or to amorphous iron silicate. However, like other silicates that we have studied, it gets better with exposure to CO, N₂ and H₂ over time: e.g., after formation of a macromolecular carbonaceous layer on the surfaces of the underlying grains. While amorphous iron silicates required only 1 or 2 experimental runs to achieve steady state reaction rates, graphite only achieved steady state after 6 or more experiments. We will present results showing the catalytic action of graphite grains increasing with increasing number of experiments and will also discuss the nature of the final "graphite" grains after completion of our experiments.

Trapping Noble Gases in the Carbonaceous Macromolecular Grain Coatings:

References: [1] Hayatsu R. and Anders, E. (1981) *Top.Curr.Chem.* 99, 1-39. [2] Hornbeck, G. (1995) *Planet.Spa.Sci* 43, 189-217. [3] Nuth, J.A., Charnley, S.B. and Johnson, N.M. (2006) in *Meteorites and the*

Early Solar System II (D.S. Lauretta and H.Y. McSween, eds.) (Univ.Ariz.Press, Tucson) pp. 147-167. [4] Ciesla, F.J. and Charnley, S.B. (2006) in *Meteorites and the Early Solar System II* (D.S. Lauretta and H.Y. McSween, eds.) (Univ.Ariz.Press, Tucson) pp. 209 - 230. [5] Fegley, B. (1993) in *The Chemistry of Life's Origins* (J.M. Greenberg, C.X. Mendoza-Gomez, and V. Pirronello, eds.) (Kluwer, Dordrecht) pp. 75 - 147. [6] Pizzarello, S. Cooper, G.W. and Flynn, G.J. (2006) in *Meteorites and the Early Solar System II* (D.S. Lauretta and H.Y. McSween, eds.) (Univ.Ariz.Press, Tucson) pp. 625 - 651. [7] Pearce, B.B. Twigg, M.V. and Woodward, C. (1989) in *Catalyst Handbook*, 2nd Ed. (M.W. Twigg, ed.) (Wolfe Pub. Ltd., London) pp. 340 - 378. [8] Hindermann, J.P. Hutchings and Kiennerman, G.J. (1993) *Cat. Rev. Sci. Eng.* 35, 1 - 127. [9] Kress, M.E. and Tielens, A.G.G.M. (2003) *MAPS* 36, 75 - 91. [10] Hill, H.G.M., Grady, C.A., Nuth, J.A., Hallenbeck, S.J. and Sitko, M.L. (2001) *Proc. Nat. Acad. Sci.* 98, 2182-2187. [11] Johnson, N.M., Steiner, M.E. and Nuth, J.A. (2007) *LPSC XXXVIII Abs.* # 2183. [12] Llorca, J. and Casanova, J. (2000) *MAPS* 35, 841-848. [13] Hill, H.G.M. and Nuth, J.A. (2003) *Astrobiology* 3, 291-304